

10/520802

11 JAN 2005

PCT/EP03/06761

Europäisches
PatentamtEuropean
Patent OfficeOffice européen
des brevets

REC'D 29 JUL 2003

WIPO

FCI

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02291772.8

**PRIORITY
DOCUMENT**SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Anmeldung Nr:
Application no.: 02291772.8
Demande no:

Anmeldetag:
Date of filing: 12.07.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
2596 HR Den Haag
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Process to prepare a heavy and a light lubricating base oil

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C10G/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

TS 5580 EPC

Crw

PROCESS TO PREPARE A HEAVY AND A LIGHT LUBRICATING BASE
OIL

The invention is directed to a process to prepare a heavy and a light lubricating base oil.

Solvent refined processes are well known to prepare base oils having the properties of residual base oils to
5 light base oils from a petroleum derived source. Light base oils are prepared by solvent refining a lower boiling vacuum distillate stream and the residual base oils are prepared by solvent refining a de-asphalted vacuum residue. Various intermediate grades can be
10 prepared from the intermediate boiling feedstocks. The resulting base oils could have a kinematic viscosity at 100 °C from 2 cSt for the light base oils to above 30 cSt for the heaviest grades.

There is a tendency in the base oil field to prepare
15 base oils which contain more saturated components, less sulphur and which have a higher viscosity index than the base oils which can be made by means of the above described solvent refining route. A very suited process is to catalytically dewax the residual fraction obtained
20 in a fuels hydrocracker process. With a fuels hydrocracker process is meant a process wherein a feedstock is hydroprocessed to mainly middle distillate fuels products. The higher boiling fraction is usually recycled to the hydrocracking step. This bottoms
25 fraction, also referred to as hydrocracker bottoms, can also be used to prepare base oils. Such a process is for example described in WO-A-9718278.

A disadvantage of the process as described above is that it has been found difficult to prepare the high viscosity product at all or in a sufficient quantity.

5 The object of the present invention is to provide a process, which can prepare at least a light and a heavy base oil.

The following process achieves this object. Process to prepare a heavy (13) and a light lubricating base oil (17) from a partly isomerised Fischer-Tropsch derived
10 feedstock (1), said feedstock having an initial boiling point of below 400 °C and a final boiling point of above 600 °C by

(a) separating, by means of distillation (2), said fraction into a light base oil precursor fraction (4) and
15 a heavy base oil precursor fraction (5),
(b) reducing the pour point of each separate base oil precursor fraction by means of dewaxing,
(c) and isolating the desired base oil products (13, 17) from said dewaxed oil fractions (9, 10) as obtained in
20 step (b).

Applicants have found that with the process according to the invention highly saturated base oils containing almost no sulphur and having a high viscosity index can be prepared. Furthermore different base oil grades may be
25 prepared using this process, ranging from the low viscosity grades to the high viscosity grades.
For example a base oil product slate, wherein the different products have kinematic viscosities at 100 °C of about 2, 5, 8.5 and 20 cSt respectively may be
30 prepared in a high yield.

Different publications disclose the preparation of Fischer-Tropsch derived base oils. However no publication has disclosed a process for the simultaneous preparation

of both low and high viscosity base oils. For example EP-A-1029029, WO-A-0014187 and EP-A-776959 describe the preparation of low viscosity grade base oil from a Fischer-Tropsch derived feed. The kinematic viscosity at 100 °C of the disclosed base oils ranged from 5.1 to 7.9 cSt. WO-A-0015736 discloses a process in which base oil is obtained from a Fischer-Tropsch derived feed having a kinematic viscosity at 100 °C of 24.89 cSt.

The preferred feed to step (a) may be suitably the heavy fraction as obtained when hydrocracking a Fischer-Tropsch synthesis product. Such a Fischer-Tropsch synthesis product will comprise mainly normal paraffins with up to and above 60 carbon atoms. This synthesis product is suitably hydroprocessed (hydroisomerisation/hydrocracking) to convert to one or more middle distillate products and a heavy, atmospheric bottoms product fraction. This heavy bottoms product fraction having an initial boiling point of below 400 °C and preferably above 300 °C and more preferably above 340 °C will comprise mainly partly isomerised paraffins. An example of a suitable hydroprocessing process for a Fischer-Tropsch synthesis product is described in EP-A-668342.

The fraction boiling above 540 °C in the feed to step (a) is preferably at least 20 wt% and more preferably at least 30 wt% and most preferably at least 40 wt%. Typically this fraction will be less than 80 wt%. Such heavy Fischer-Tropsch derived feeds may be obtained when a relatively heavy Fischer-Tropsch synthesis product is hydrocracked. Not all Fischer-Tropsch synthesis processes yield such a heavy product. A preferred Fischer-Tropsch process on which product the feed for the

present invention can be based is described
in WO-A-9934917 and in AU-A-698392.

5 In step (a) the feed is separated by means of
distillation into a light base oil precursor fraction and
a heavy base oil precursor fraction. The distillation is
suitably performed at low (vacuum) pressures, more
preferably the vacuum distillation is performed at a
pressure of between 0.01 and 0.1 bara. Preferably the
effective cut temperature in step (a) at which the light
10 and heavy base oil precursor fractions are separated is
between 470 and 600 °C and more preferably between
480 and 580 °C. Suitably the feed is separated into two
base oil precursor fractions. Separation into more base
oil precursor fractions is also possible. A lower boiling
15 fraction, boiling in the vacuum gas oil range, may also
be obtained in the distillation of step (a) and may be
used as gas oil (blending) component or technical
white oil.

20 Step (b) may be performed by means of solvent
dewaxing or catalytic dewaxing. Solvent dewaxing is well
known to those skilled in the art and involves admixture
of one or more solvents and/or wax precipitating agents
with the base oil precursor fraction and cooling the
mixture to a temperature in the range of
25 from -10 °C to -40 °C, preferably in the range of
from -20 °C to -35 °C, to separate the wax from the oil.
The oil containing the wax is usually filtered through a
filter cloth which can be made of textile fibres, such as
cotton; porous metal cloth; or cloth made of synthetic
30 materials. Examples of solvents which may be employed in
the solvent dewaxing process are C₃-C₆ ketones
(e.g. methyl ethyl ketone, methyl isobutyl ketone and
mixtures thereof), C₆-C₁₀ aromatic hydrocarbons

(e.g. toluene), mixtures of ketones and aromatics (e.g. methyl ethyl ketone and toluene), autorefrigerative solvents such as liquefied, normally gaseous C₂-C₄ hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof. Mixtures of methyl ethyl ketone and toluene or methyl ethyl ketone and methyl isobutyl ketone are generally preferred. Examples of these and other suitable solvent dewaxing processes are described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994, Chapter 7.

Preferably step (b) is performed by means of a catalytic dewaxing process. The catalytic dewaxing process may be any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal.

Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Pt/ZSM-35, Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable
5 molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-4343692, US-A-5053373, US-A-5252527 and US-A-4574043.

The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally
10 occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are:
15 alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a
20 low acidity refractory oxide binder material, which is essentially free of alumina, is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most
25 preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein
30 the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by

contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-0029511. Examples of suitable dewaxing catalysts as described
5 above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-0029511 and EP-B-832171.

10 More preferably the molecular sieve is a MTW, MTT or TON type molecular sieve, of which examples are described above, the Group VIII metal is platinum or palladium and the binder is silica.

15 Preferably the catalytic dewaxing of the heavy base oil precursor fraction is performed in the presence of a catalyst as described above wherein the zeolite has at least one channel with pores formed by 12-member rings containing 12 oxygen atoms. Preferred zeolites having 12-member rings are of the MOR type, MTW type, FAU type,
20 or of the BEA type (according to the framework type code). Preferably a MTW type, for example ZSM-12, zeolite is used. A preferred MTW type zeolite containing catalyst also comprises as a platinum or palladium metal as Group VIII metal and a silica binder. More preferably
25 the catalyst is a silica bound AHS treated Pt/ZSM-12 containing catalyst as described above. These 12-member ring type zeolite based catalysts are preferred because they have been found to be suitable to convert waxy paraffinic compounds to less waxy iso-paraffinic
30 compounds.

More preferably the above described catalyst comprising the 12-member ring zeolite is used in a first hydroconversion step to lower the pour point of the base

oil precursor to a intermediate value between the pour point of the feed and the pour point of the final base oil. More preferably the pour point of the intermediate product is between -10 to +10 °C. The process conditions of such a first step may be suitably the catalytic dewaxing conditions as described below. This first hydroconversion step is followed by a final dewaxing step wherein preferably a catalyst is used which comprises a zeolite having at least one channel with pores formed by 10-member rings containing 10 oxygen atoms. Suitably as 10-member ring zeolites one of the following list comprising a TON type, MFI type, MTT type or FER type is used. The specific catalyst may be one as disclosed above which are according to these zeolite types. A preferred 10-member ring zeolite containing catalyst will also comprise a platinum or palladium metal as Group VIII metal and a silica binder. More preferably the catalyst is a silica bound AHS treated Pt/ZSM-5 or a silica bound AHS treated Pt/ZSM-23 containing catalyst as described above.

In an even more preferred embodiment also the light base oil precursor fraction is catalytic dewaxed as described above for the heavy base oil precursor fraction.

Applicants have found that the two-step process as described above for reducing the pour point may also be used in processes to prepare base oils having a pour point of suitably below -15 °C, more preferably below -20 °C, from a feedstock comprising between 30 and 100 wt% wax, preferably between 50 and 100 wt% wax. The wax content is defined as the wax content which is recovered by solvent dewaxing at -27 °C in a standard methyl-ethylketone toluene mixture.

Such a feedstock may be obtained in a Fischer-Tropsch process such as for example described above. Other suitable feedstocks are the residual fraction obtained in a fuels hydrocracker process or a (hydrotreated) slack wax.

5

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil.

10

15

By varying the temperature between 275, suitably between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably +10 °C for the heavier grades to as far down to -60 °C for the lighter grades.

20

In step (c) the effluents of the separate dewaxing steps are separated by means of distillation into at least a light and heavy base oil grade. The distillation is suitably performed at low (vacuum) pressures, more preferably the vacuum distillation is performed at a pressure of between 0.01 and 0.1 bara. Preferably the effective cut temperature in step (c) at which the light and heavy base oil fractions are separated is between 470 and 600 °C and more preferably between 480 and 540 °C. Step (c) is preferably performed in one distillation column. Line-ups wherein two or more

25

30

vacuum distillations columns are used could also be envisaged.

5 The invention shall be illustrated by making use of Figure 1 and 2. Figure 1 shows an example of a preferred embodiment of the process according to the present invention. Figure 2 shows the process of Figure 1 except that two product vacuum distillation columns are used.

10 In Figure 1 a Fischer-Tropsch derived feedstock (1) is fed to a vacuum distillation column (2). In this column the feed (1) is separated into a vacuum gas oil fraction (3), a light base oil precursor fraction (4) and a heavy base oil precursor fraction (5). The viscosity of the targeted base oils will depend on the viscosity of the base oil precursor fractions (4,5). The desired
15 viscosity of these precursor fractions may be obtained by manipulating the distillate cut point in step (a).

In Figure 1 the catalytic dewaxing step (b) is performed in two parallel operating catalytic dewaxing reactors (7,8). Alternatively one solvent or catalytic
20 dewaxing reactor may also be used, wherein base oil precursor fractions (4,5) are processed alternatively (in a so-called blocked out mode). The latter operation requires less reactors but on the other hand requires more intermediate storage and operational changes.
25 Thus preferably two parallel-operated dewaxing reactors are used. In this manner dedicated dewaxing catalysts, in case catalytic dewaxing is used, may be advantageously used.

30 The effluents (9, 10) of the dewaxing step (b) as performed on fractions (4,5) are separated in one distillation column (14) In column (14) various base oil grades (16, 17, 13) may obtained after topping off the lower boiling fraction (15). Applicants have found that

it is now possible to simultaneously obtain at least a light base oil grade (16) having a kinematic viscosity at 100 °C of about 3.8 to 6 cSt which can be used in motor lubricant formulations, and a heavy base oil grade. In Figure 1 two heavy base oil grades are illustrated. Line-ups wherein only one heavy base oil grade is prepared are also possible. The heavy base oil grade (17) preferably has a kinematic viscosity at 100 °C of between 7 to 15 cSt. This base oil grade may be used as technical or medicinal white oil. A second heavy base oil grade (13) is also separated in column (14) having preferably a kinematic viscosity at 100 °C of above 15 cSt, more preferably above 17 cSt and even more preferably above 20 cSt. It may be advantageous to recycle part of the heavy grade (13) to the catalytic dewaxing reactor (8) in order to control the quality of said heavy base oil grade (13). In column (14) more grades (not shown) may be obtained having a kinematic viscosity at 100 °C of between 2 and 4 cSt. The top fraction (15) boiling below the base oil grades can be used as fuel (gas oil, kerosene, naphtha, LPG) blending component.

In Figure 2 the effluent (10) is first separated in a heavy base oil column (11) into the heavy base oil (13) as described above and a lower boiling fraction (12). This lower boiling fraction (12) is preferably supplied to the base oil distillation column (14) as shown, fed to reactor (7) or to vacuum distillation column (2). The viscosity of the heavy base oil grade (17) may be controlled by adjusting the cut point in distillation column (2). Alternatively the viscosity of base oil grade (17) may be adjusted by adding some of the heavy

base oil fraction (6) to the light base oil precursor fraction (4) before performing step (b).

In this application reference is made to kinematic viscosity as measured by ASTM D 445 and to pour point as measured by ASTM D 97-93.

C L A I M S

1. Process to prepare a heavy and a light lubricating base oil from a partly isomerised Fischer-Tropsch derived feedstock (1), said feedstock having an initial boiling point of below 400 °C and a final boiling point of
5 above 600 °C by
 - (a) separating, by means of distillation , said fraction into a light base oil precursor fraction and a heavy base oil precursor fraction,
 - (b) reducing the pour point of each separate base oil
10 precursor fraction by means of dewaxing,
 - (c) and isolating the desired base oil products from said dewaxed oil fractions as obtained in step (b).
2. Process according to claim 1, wherein the effective cut temperature in step (a) at which the light and heavy
15 (5) base oil precursor fractions are separated is between 470 and 600 °C.
3. Process according to any one of claims 1-2, wherein the fraction boiling above 540 °C in the feed to step (a) is at least 20 wt%.
- 20 4. Process according to claim 3, wherein the fraction boiling above 540 °C in the feed to step (a) is at least 30 wt%.
5. Process according to any one of claims 1-4, wherein the heavy base oil as obtained in step (c) has a
25 kinematic viscosity at 100 °C of above 15 cSt, preferably above 17 cSt and more preferably above 20 cSt.
6. Process according to claim 5, wherein a base oil having a kinematic viscosity at 100 °C of between 7 and 15 cSt is isolated from the dewaxed light base oil
30 precursor fraction.

7. Process according to any one of claims 1-6, wherein the light base oil as obtained in step (c) has a kinematic viscosity at 100 °C of between 3.8 and 6 cSt.
8. Process according to any one of claims 1-7, wherein the dewaxing of the heavy and light base oil precursor fraction is performed simultaneously in two different reactors.
9. Process according to any one of claims 1-8, wherein the dewaxing step is performed by means of a catalytic dewaxing process in the presence of a catalyst comprising a medium pore size molecular sieve and a Group VIII metal.
10. Process according to claim 9, wherein the molecular sieve is a MTW, MTT or TON type molecular sieve.
11. Process according to any one of claims 9 or 10, wherein the Group VIII metal is platinum or palladium.
12. Process according to any one of claims 9-11, wherein the catalyst used in the catalytic dewaxing of the heavy base oil precursor fraction comprises a MTW molecular sieve, platinum or palladium as Group VIII metal and a silica binder.
13. Process according to claim 12, wherein the catalytic dewaxing of both light and heavy base oil precursor fractions are performed in the presence of a catalyst comprising a MTW molecular sieve, platinum or palladium as Group VIII metal and a silica binder.
14. Process according to any one of claims 1-8, wherein the heavy base oil precursor fraction is reduced in pour point by first performing a pour point reducing step in the presence of a catalyst comprising a 12-member ring zeolite and secondly performing a catalytic dewaxing on the effluent of the first step in the presence of a 10-member ring zeolite.

- 15 -

15. Process according to claim 14, wherein the pour point after the first dewaxing step is between -10 and +10 °C.

BS1/TS5580PD

A B S T R A C T

PROCESS TO PREPARE A HEAVY AND A LIGHT LUBRICATING BASE
OIL

Process to prepare a heavy and a light lubricating base oil from a partly isomerised Fischer-Tropsch derived feedstock (1), said feedstock having an initial boiling point of below 400 °C and a final boiling point of above 600 °C by

- (a) separating, by means of distillation , said fraction into a light base oil precursor fraction and a heavy base oil precursor fraction,
- (b) reducing the pour point of each separate base oil precursor fraction by means of dewaxing,
- (c) and isolating the desired base oil products from said dewaxed oil fractions as obtained in step (b).

TS SSB EPC

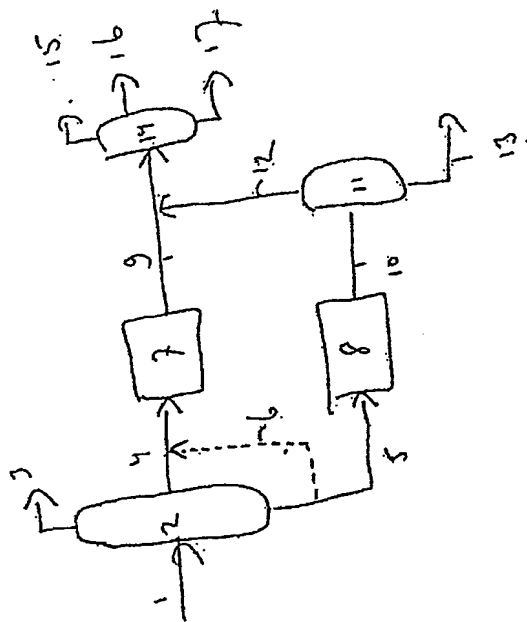


Fig. 2

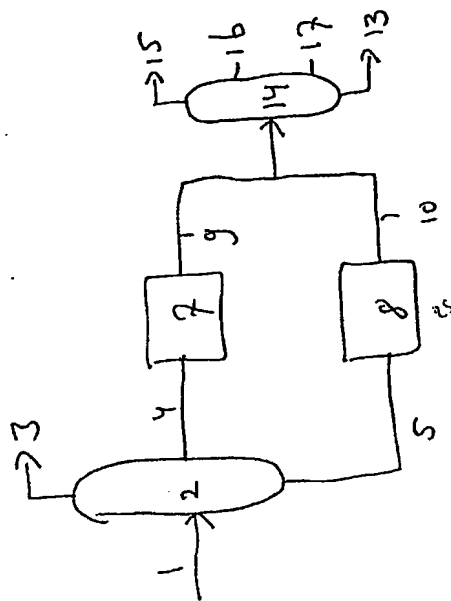


Fig. 1